



Vinyl Ester Polymer Electrolytes for Multifunctional Composites

**by James F. Snyder, Matthew J. Hagon, Rob H. Carter,
and Eric D. Wetzel**

ARL-RP-191

September 2007

*A reprint from Proceedings of the American Chemical Society Division of Polymeric Materials:
Science & Engineering (PMSE Preprints), Vol. 93, Fall 2005,
Washington, D.C., 28 August – 1 September 2005.*

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

ARL-RP-191**September 2007**

Vinyl Ester Polymer Electrolytes for Multifunctional Composites

**James F. Snyder, Matthew J. Hagon, Rob H. Carter,
and Eric D. Wetzel**

*U.S. Army Research Laboratory
Weapons and Materials Research Directorate*

A reprint from *Proceedings of the American Chemical Society Division of Polymeric Materials:
Science & Engineering (PMSE Preprints)*, Vol. 93, Fall 2005,
Washington, D.C., 28 August – 1 September 2005.

| | | | | | |
|--|-------------------------|----------------------------------|---|-------------------------------------|--|
| REPORT DOCUMENTATION PAGE | | | <i>Form Approved</i> OMB No. 0704-0188 | | |
| <p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p> | | | | | |
| 1. REPORT DATE (DD-MM-YYYY) September 2007 | | 2. REPORT TYPE Reprint | | 3. DATES COVERED (From - To) | |
| 4. TITLE AND SUBTITLE Vinyl Ester Polymer Electrolytes for Multifunctional Composites | | | 5a. CONTRACT NUMBER | | |
| | | | 5b. GRANT NUMBER | | |
| | | | 5c. PROGRAM ELEMENT NUMBER | | |
| 6. AUTHOR(S) James F. Snyder, Matthew J. Hagon, Rob H. Carter, and Eric D. Wetzel | | | 5d. PROJECT NUMBER | | |
| | | | 5e. TASK NUMBER | | |
| | | | 5f. WORK UNIT NUMBER | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-MA Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD, 21005-5069. | | | 8. PERFORMING ORGANIZATION REPORT NUMBER ARL-RP-191 | | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197 | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | | |
| | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) ARL-RP-191 | | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT <p>This report is a reprint of a paper published in <i>Proceedings of the American Chemical Society Division of Polymeric Materials: Science & Engineering (PMSE Preprints)</i>, Vol. 93, Fall 2005 by the American Chemical Society.</p> <p>Polymer electrolytes have potential for use in solid state electrochemical devices owing to favorable material properties. We have developed a multifunctional concept for material development that integrates structural performance with energy storage. One focus of our research is to develop polymer electrolytes that exhibit a desirable combination of mechanical strength and ion conductivity. In the present study, PEG vinyl esters were complexed with lithium triflate and studied as both homopolymer and random copolymer electrolytes. Lithium content was first optimized on a diverse sampling of the set through varied salt concentrations. Homopolymer electrolytes at 30 EO:Li were then characterized. The homopolymers vary in length of PEG oligomers, number of vinyl esters per monomer, and additional functionality. Random copolymer electrolytes were investigated using electrochemically strong monomers and mechanically strong monomers in systematically varied weight percent. The resulting electrochemical and mechanical properties will be discussed as well as the directions of future research.</p> | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT SAR | 18. NUMBER OF PAGES 8 | 19a. NAME OF RESPONSIBLE PERSON James F. Snyder |
| a. REPORT U | b. ABSTRACT U | c. THIS PAGE U | | | 19b. TELEPHONE NUMBER (Include area code) (410) 306-0842 |

Vinyl Ester Polymer Electrolytes for Multifunctional Composites

James F. Snyder, Matthew J. Hagon, Robert H. Carter, and Eric D. Wetzel

Army Research Laboratory, Materials Division, Aberdeen Proving Ground, MD.

INTRODUCTION

A number of electrochemical devices, in particular lithium batteries, utilize polymers in constructing the electrolyte layer. Typically these materials comprise ion conducting polymers or polymer gels that are easily deformable but dimensionally sound membranes. These solid state materials can serve as both the electrolyte and the separator between electrodes but they possess limited mechanical properties. Achieving improved mechanical properties is often hindered by the competing need for polymer mobility to aid ion transport in solvent-free systems, as well as the breakdown in mechanical properties in solvent swollen systems. Previous methods to maintain desirable structural properties in polymer electrolytes have included crosslinking¹, ceramic particle and fiber fillers^{2,3}, and block arrangement of copolymers⁴, among other efforts. However, research into these methods typically falls short of reaching superior mechanical properties while maintaining useful ion conductivity.

We are developing polymer electrolytes with a principal focus on mechanical properties, in particular high stiffness values (>100 MPa) as well as convenient processing. Our projected applications include multifunctional structural batteries that could potentially replace inert structural components, such as unmanned aerial vehicle (UAV) wings.⁵ Within this scope, the primary need is for a mechanically robust electrolyte that can function as a structural material while providing sufficient ion transport. The present study includes solvent-free ion conducting vinyl ester resins.

EXPERIMENTAL

Materials. Lithium triflate (Aldrich) was dried at 180 °C under vacuum for 8 h. Sartomer Company supplied acrylate and methacrylate functionalized monomer samples. The monomers were stored between uses in a refrigerator in brown glass bottles sealed with parafilm. Chemicals were used as received and handled under dry nitrogen.

Polymer Synthesis. Lithium triflate was added to the appropriate PEG acrylate or methacrylate functionalized monomer to achieve the desired salt content. The components were sealed in a glass vial, mixed on a roll mixer and/or vortexer, and gently heated (< 80 °C) as necessary to fully dissolve the salt. Light exposure was minimized during this process. Thermally induced polymerization was not apparent in the absence of initiator. The solutions were degassed in a vacuum oven at 60 °C until bubbling had ceased. Copolymer formulations were mixed in 4 mL glass vials at the desired ratio of monomers. Organic peroxide with the trade name Trigonox was added as the initiator in quantity 1.5 wt% (vs. resin), followed by 1 wt% (vs. resin) dimethylaniline. The samples were mixed thoroughly with a spatula and poured into silicone rubber molds. The molds were heated under continuous nitrogen purge to 80 °C for 12 h, followed by 110 °C for 1 h, after which the oven was allowed to cool to room temperature.

The cured pellets, measuring 12.3 mm in diameter and 3 mm in thickness, were measured precisely using a digital caliper. Both sides of the pellets were coated with a thin application of quick drying silver paint followed by heat treatment (90-110°C) under vacuum for at least 12 h to remove residual solvent. The superficial films were measured to be about 0.03 mm thick. Each pellet was used for both electrochemical and mechanical testing.

Characterization. Electrochemical impedance spectroscopy was conducted using a Solartron 1260 Impedance / Gain-Phase Analyzer and Solartron 1287 Electrochemical Interface across a frequency range of 106 Hz to 10 Hz at room temperature (18 - 20 °C). Each

sample was assembled under a dry air atmosphere in a test cell with stainless steel blocking electrodes. For mechanical characterization, compression testing was conducted at room temperature using a MTS load frame with a 5 kN load cell. Each sample was exposed to standard atmosphere for two minutes during compression. The tests were run in a displacement control mode at a cross-head speed of 1 mm/min. Data was normalized for error resulting from system compliance.

RESULTS AND DISCUSSION

An outline of the polymer materials used in this study is included in Table 1. Polyacrylates have been previously studied for electrolyte use owing to their dimensional stability, however they are typically plasticized.⁶ A diverse sampling of PEG vinyl ester monomers were initially mixed with lithium triflate in a concentration range of 10 – 50 EO:Li (etheric oxygens per lithium) to ascertain the optimal salt concentration for each sample as determined by solvent-free conductivity values. Some of the conductivity data is presented in Figure 1 and indicates peak conductivity at 30 – 40 EO:Li, which corresponds to about 9-12 wt% salt with respect to PEG. Note that the concentration of PEG in these samples ranges between 60 wt% - 70 wt%, but these variations present no substantial difference in the absolute concentration of the salt

Table 1. Structural Electrolyte Material Components

| Matrix Element | Description |
|----------------|----------------------------------|
| Linear | Polyacrylate with PEG sidechains |
| Networked | PEG Diacrylate |
| | PEG Triacrylate |
| | PEG Tetraacrylate |

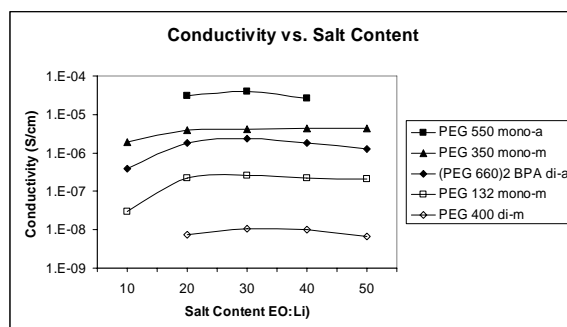


Figure 1. Conductivity vs. salt content for solvent-free vinyl ester polymer electrolyte. "Mono-" resins form comb polymers while "di-" resins form networked polymers. "a" and "m" in the legends refer to "acrylate" and "methacrylate", respectively.

A more comprehensive set of PEG vinyl ester monomers was then complexed with lithium triflate at 30 EO:Li and polymerized as homopolymers. The homopolymers systematically vary in length of the PEG oligomer, number of vinyl ester functional groups per monomer, and the nature of additional functional groups. Figures 2 and 3 relate the modulus and conductivity data for the homopolymer electrolytes as a function of concentration vinyl groups and PEG, respectively. In these materials, the vinyl groups are the means by which polymer growth and crosslink formation occur and PEG oligomers control ion diffusion. In Figure 2, not all vinyl groups may be considered to have reacted, especially for networked species that have reached the gel point.⁷ However, a trend is evident for each type of monomer, and PEG mono-, di-, tri-, and tetraacrylates are all fit by a power law as shown in the figure. This suggests that it may be possible to predict the properties of similar acrylic PEG electrolytes not tested here. Trends are also apparent in Figure 3 for conductivity vs. PEG

concentration, although the asymptotic behavior at low concentrations of PEG prohibits a predictive regression analysis. However, this asymptotic behavior may be an artifact of our inability to accurately measure very low conductivity values. Experiments are underway to resolve conductivity data below 10^{-7} S/cm.

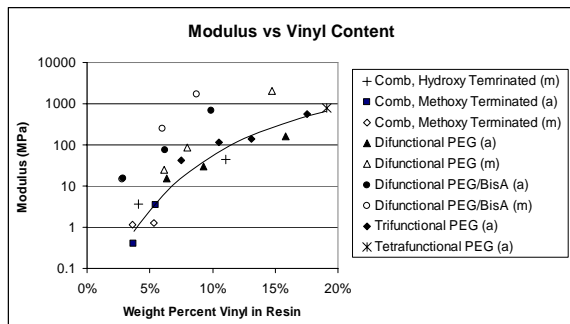


Figure 2. Modulus trends for solvent-free vinyl ester polymer electrolytes as perceived through vinyl concentration. A best fit power law regression is included for PEG acrylates, $y = 721000x^{4.13}$ ($R=0.94$). The vinyl concentration includes all available vinyl groups based on molecular structure. “a” and “m” in the legends refer to “acrylate” and “methacrylate”, respectively.

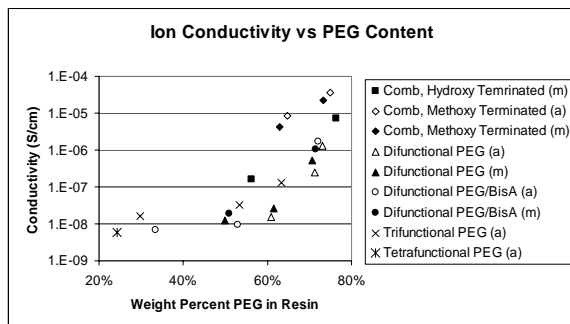


Figure 3. Conductivity trends with decreasing PEG oligomer lengths for solvent-free vinyl ester polymer electrolytes as perceived through increasing weight percent PEG. “a” and “m” in the legends refer to “acrylate” and “methacrylate”, respectively.

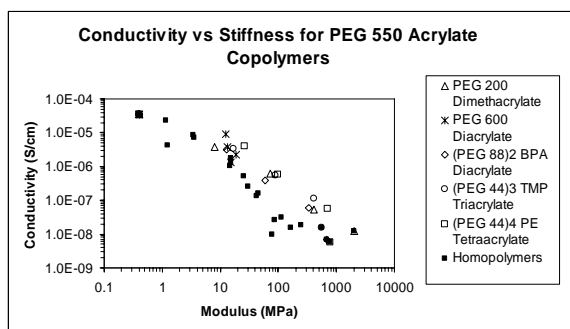


Figure 4. Electrochemical and mechanical behavior for homopolymers (solid markers) and select copolymers (open markers) of PEG vinyl ester electrolytes.

Monomers of four of the comb homopolymers that showed electrochemically promising results were subsequently mixed in approximately 25 wt%, 50 wt%, and 75 wt% with monomers of the crosslinking resins to form random copolymer electrolytes. Figure 4 illustrates the difference in combined electrochemical / mechanical behavior between the homopolymers and some of the copolymers.

Samples that appear towards the upper right corner of the graph are considered the most useful since they perform well in both categories. The copolymers typically outperformed the homopolymer trend, and were noticeably better than the average of the two homopolymers comprising them. It is possible that performance may be further enhanced by controlling monomer reactivity into block architecture.

While samples described here do not have the necessary performance characteristics for highly efficient composite application, the trends elucidated through these studies do indicate directions for continuing material development. In addition, parallel work has been performed in our laboratory in which functioning structural batteries have been fabricated using the materials described here.

ACKNOWLEDGEMENTS

The authors wish to thank R. Jow and K. Xu (Battery Team, ARL) for useful conversations and continued assistance with electrochemical measurements. We also wish to acknowledge Corydon Hilton for assistance with mechanical testing.

REFERENCES

1. Le Nest, J. F.; Gandini, A.; Cheradame, H. *Br. Polym. J.* **1988**, *20*, 253.
2. Scrosati, B.; Croce, F.; Panero, S. *J. Power Sources*, **2001**, *100*, 93.
3. Wen, Z.; Wu, M.; Itoh, T.; Kubo, M.; Lin, Z.; Yamamoto, O. *Solid State Ionics*, **2002**, *148*, 185.
4. Soo, P. P.; Huang, B.; Jang, Y.-I.; Chiang, Y.-M.; Sadoway, D.; Mayes, A. M. *J. Electrochem. Soc.*, **1999**, *146*, 32.
5. Thomas, J. P.; Muhammad, A. Q. *Acta Materialia*, **2004**, *52*, 2155.
6. Kono, M.; Hayashi, E.; Nishiura, M.; Watanabe, M. *J. Electrochem. Soc.*, **2000**, *147*, 2517.
7. Flory, P. J. In *Principles of Polymers Chemistry*, Cornell University Press: Ithaca, 1953, p.p. 347-398.

Distribution List

ADMNSTR 1 elec
DEFNS TECHL INFO CTR
DTIC OCP (ELECTRONIC COPY)
8725 JOHN J KINGMAN RD STE 0944
FT BELVOIR VA 22060-6218

US ARMY RSRCH LAB 6
IMNE ALC IMS MAIL & RECORDS MGMT
AMSRD ARL D J M MILLER
AMSRD ARL CI OK TL TECHL LIB (2 COPIES)
AMSRD ARL CI OK T TECHL PUB (2 COPIES)
2800 POWDER MILL ROAD
ADELPHI MD 20783-1197

US ARMY RESEARCH LAB 1
AMSRD CI OK TP TECHL LIB
ATTN T LANDFRIED
APG MD 21005

US ARMY RESEARCH LAB 6
AMSRD ARL WM MA
J SNYDER (3 COPIES)
P NGUYEN
E WONG
AMSRD ARL WM MB
R CARTER
BUILDING 4600
APG MD 21005-5069

TOTAL 14 (1 Electronic, 13 HCs)

INTENTIONALLY LEFT BLANK.